Hierarchical mesoporous $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid nanowire arrays supported on Ni foam for high-performance asymmetric supercapacitors

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ABSTRACT In this paper, hierarchical mesoporous $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid nanowire arrays (NWAs) on Ni foam were prepared through a two-step hydrothermal process associated with successive annealing treatment. The $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs exhibited excellent electrochemical performances with a high specific capacity of $1,240.5 \text{ C g}^{-1}$ at a current density of 2 mA cm^{-2} , with rate capability of 59.0% shifting from 2 to 30 mA cm^{-2} , and only a 9.1% loss of its capacity even after 3,000 cycles at a consistent current density of 10 mA cm^{-2} . An asymmetric supercapacitor ($\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ NWAs||activated carbon) was fabricated and exhibited a high specific capacity of 168 C g^{-1} at a current density of 1 A g^{-1} . And a preferable energy density of 37.3 Wh kg^{-1} at a power density of 800 W kg^{-1} was obtained. The excellent electrochemical performances indicate the promising potential application of the hierarchical mesoporous $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs in energy storage field.

Keywords: $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$, nanowire arrays, specific capacity, asymmetric supercapacitor

INTRODUCTION

The increasingly serious environmental problems associated with fossil fuels have prompted intense research interest into the development of sustainable and reliable energy storage systems. Among a wide variety of innovative energy storage systems, supercapacitors have attracted significant research attention in recent years due to high power density, excellent reversibility and long cycle life for time-dependent power needs of modern electronics and power systems [1–3]. The key to high energy densities is developing novel electrode materials with high specific capacities at high operating voltages [4]. Currently, many researches focus on the rational

design of novel electrode materials with high capacity, large energy density and long cycling stability [5–7]. Generally, electrode materials can be divided into three categories: carbon materials [8–10], conductive polymer materials [11–14], and transition metal oxides (TMOs) (MnO_2 , NiO , Co_3O_4 , NiCo_2O_4 , ZnCo_2O_4 , etc.) [15–21]. Among the candidate electrode materials, TMOs have higher specific capacity and energy density than carbon-based materials and more excellent chemical stability than conductive polymer materials, considered as a promising choice for the supercapacitors.

Among numerous TMOs, Co_3O_4 with a spinel structure can be considered as one of the best alternative material due to its environmental friendliness, high theoretical capacity, controllable size and shape, tunable surface and structural properties, good electrochemical performance in alkaline solutions due to its ability to interact with electrolyte ions not only at the surface, but also throughout the bulk, low cost and favorable Faraday characteristics [22–25]. Xia *et al.* [26] fabricated hollow Co_3O_4 nanowire arrays (NWAs) by seed mediated hydrothermal method which showed a specific capacitance of 599 F g^{-1} at a constant current density of 2 A g^{-1} . In another report, Rakhi *et al.* [27] reported that Co_3O_4 nanowires with brush-like and flower-like morphologies exhibited specific capacitance values of $1,525 \text{ F g}^{-1}$ and $1,199 \text{ F g}^{-1}$, respectively, at a constant current density of 1 A g^{-1} . Unfortunately, in all these cases the observed specific capacitances are much less than the theoretical value of $3,560 \text{ F g}^{-1}$, especially at high current densities, as the active materials are typically too insulating to support fast electron transport at high current densities. Compared with single TMOs, binary TMOs have attracted great research interest as electrode materials for high

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performance pseudocapacitors due to their multiple redox reactions and high electrical conductivity. ZnCo_2O_4 with a typical spinel structure, as one of the most attractive electrode materials, where the Zn^{2+} occupies the tetrahedral sites and the Co^{3+} occupies the octahedral sites, has been widely studied as a high-performance electrode material for supercapacitors [28–30]. It has a better electrical conductivity compared with Co_3O_4 , and exhibits excellent rate capability and cycling stability. It was reported that core-shell hybrid nanostructures had better properties (e.g., superior cycling stability), and coating the grown wires or tubes with smaller, porous nanosized structures enhanced the electrochemical properties further [31–34]. As a consequence, the design and fabrication of Co_3O_4 and ZnCo_2O_4 hybrid electrode with the well-designed architecture is expected to obtain higher performance supercapacitors.

Herein, we reported that hierarchical mesoporous $\text{Co}_3\text{O}_4@ \text{ZnCo}_2\text{O}_4$ hybrid NWAs were directly grown on Ni foam as a free-standing electrode *via* a two-step approach, which involved hydrothermal and annealing treatment. Mesoporous Co_3O_4 NWAs were grown on the Ni foam as the core and ZnCo_2O_4 layer were further firmly attached to the NWAs as the shell to form a hierarchical mesoporous $\text{Co}_3\text{O}_4@ \text{ZnCo}_2\text{O}_4$ hybrid NWAs. Such unique architecture grown on the Ni foam provides high contact between the substrate and the electrode active material, which would shorten the diffusion path of electrons and ions and obtain a low contact resistance, endowing the hierarchical mesoporous $\text{Co}_3\text{O}_4@ \text{ZnCo}_2\text{O}_4$ hybrid NWAs electrode with an excellent capacitive performance. The $\text{Co}_3\text{O}_4@ \text{ZnCo}_2\text{O}_4$ NWAs hybrid electrode exhibited a high capacity of $1,240.5 \text{ C g}^{-1}$ at a current density of 2 mA cm^{-2} , satisfied rate capability of 59.0% capacity retention at 30 mA cm^{-2} , and good cycling stability of 90.9% capacitance retention over 3,000 charge-discharge cycles at a consistent current density of 10 mA cm^{-2} . In addition, a preferable energy density of 37.3 W h kg^{-1} at a power density of 800 W kg^{-1} was obtained in a two-electrode system. This work introduces a facile strategy for designing and fabricating hierarchical mesoporous TMOs based hybrid electrode with desirable energy storage performance for supercapacitors.

EXPERIMENTAL SECTION

Materials

The nickel foam was purchased from Kunshan Jiayisheng Electronics Co., Ltd (China) with a thickness of 1.5 mm, 98.0% porosity and pore rate greater than or equal to

98.0%. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NH_4F and $\text{CO}(\text{NH}_2)_2$ were all purchased from Aladdin. All reagents used in the experiment were of analytical grade and were used as received without further purification. Besides, activated carbon (AC) was purchased from Kuraray (Shanghai) Co., Ltd.

Preparation of Co_3O_4 NWAs on Ni foam

Co_3O_4 NWAs were synthesized on Ni foam by a hydrothermal process followed an annealing treatment. In a typical procedure, 3.0 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 6.0 mmol NH_4F and 15.0 mmol $\text{CO}(\text{NH}_2)_2$ were dissolved in 30 mL deionized water. A fresh Ni foam of $1 \times 4 \text{ cm}$ size was used as a substrate and it was carefully treated with acetone, 1 mol L^{-1} HCl, deionized water and ethanol in an ultrasound bath for 20 min, respectively. The obtained pink solution and the cleaned Ni foam were transferred into a 50 mL Teflon-lined stainless steel autoclave and heated to 120°C for 4 h in an oven. After cooling to room temperature, the pink product was washed with deionized water and ethanol for several times and dried at 60°C for 12 h under vacuum to obtain the precursor grown on Ni foam. Finally the precursor was annealed at 350°C for 2 h in air at a heating rate of 5°C min^{-1} to obtain Co_3O_4 NWAs electrode.

Preparation of $\text{Co}_3\text{O}_4@ \text{ZnCo}_2\text{O}_4$ hybrid NWAs on Ni foam

The as-prepared Co_3O_4 NWAs mentioned above was used as the scaffold for the synthesis of $\text{Co}_3\text{O}_4@ \text{ZnCo}_2\text{O}_4$ hybrid NWAs *via* a hydrothermal method. Typically, 1.0 mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.0 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 6.0 mmol NH_4F and 15.0 mmol $\text{CO}(\text{NH}_2)_2$ were dissolved in 30 mL deionized water to form a clear solution. Afterwards, the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave containing the as-synthesized Co_3O_4 NWAs. Then the autoclave was sealed and maintained at 120°C for 4 h. Finally, the pink precursor was obtained by rinsing with deionized water and ethanol. The $\text{Co}_3\text{O}_4@ \text{ZnCo}_2\text{O}_4$ hybrid NWAs electrode was obtained by annealing the above precursor at 350°C for 2 h.

Characterization

The X-ray diffraction (XRD) patterns were collected on a Pananalytical X-pert power with Cu K α radiation ($\lambda=1.5418 \text{ \AA}$). Scanning electron microscopy (SEM) images were observed on a JEOL JSM-6360 microscope and the energy dispersive X-ray spectroscopy (EDS) was characterized on an EDS detector system attached to JEOL JSM-6360. Transmission electron microscopy

(TEM) images were observed on a JEM-1400 operating at 100 kV (JEOL Ltd.). Nitrogen adsorption-desorption isotherms were tested at 77 K in N₂ on a QUADRASORB SI (Quantachrome) sorption analyzer. High-resolution TEM (HRTEM) and the scanning transmission electron microscopy-EDS (S/TEM-EDS) images were obtained on a Talos F200X with an accelerating voltage of 200 kV.

Electrochemical measurements

The electrochemical measurements were carried out using a CHI 660E electrochemical workstation in a three-electrode electrochemical cell at room temperature. The Co₃O₄ NWAs and Co₃O₄@ZnCo₂O₄ hybrid NWAs on Ni foam (1 cm×1 cm) electrodes were directly used as the working electrodes. The mass loadings of Co₃O₄ NWAs and Co₃O₄@ZnCo₂O₄ hybrid NWAs on Ni foam were around 1.0 and 2.4 mg cm⁻², respectively. Based on this value, the mass ratio of the Co₃O₄ to ZnCo₂O₄ in the Co₃O₄@ZnCo₂O₄ hybrid NWAs is 0.71. Hg/HgO (1.0 mol L⁻¹ KOH) reference electrode was used as the reference electrode, and the counter electrode was a Pt foil. 2 mol L⁻¹ KOH aqueous solution was used as the electrolyte. Cyclic voltammetry (CV) was conducted at various scan rates ranging from 5 to 50 mV s⁻¹ at a potential window from 0 to 0.6 V (vs. Hg/HgO). Galvanostatic charge-discharge (GCD) was measured within the range of 0 to 0.55 V at different current densities. Electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an alternating current voltage of 5 mV amplitude with a frequency range from 0.01 Hz to 100 kHz at open circuit potential. All specific capacities (Q , C g⁻¹) were calculated according to $Q = I \times \Delta t / m$ (Equation (1)) [35], where I (A) is the constant discharge current, Δt (s) is the discharge time, and m (g) is the mass of the electrode material on Ni foam.

Fabrication of the asymmetric supercapacitors

Co₃O₄@ZnCo₂O₄ hybrid NWAs and AC were used as cathode and anode electrode materials, respectively, for the fabrication of the Co₃O₄@ZnCo₂O₄||AC asymmetric supercapacitors (Co₃O₄@ZnCo₂O₄||AC ASCs). For AC electrodes, the working electrode was fabricated by mixing the AC, conducting carbon and polyvinylidene fluoride (PVDF) in a weight ratio of 75:15:10, and then casted onto a pre-cleaned Ni foam substrate with an area of 1.0 cm×1.0 cm. The coated Ni foam was vacuum dried at 60°C for 12 h. The electrochemical properties of ASCs were investigated in a two-electrode cell configuration containing 2 mol L⁻¹ KOH aqueous solution on a CHI 660E electrochemical workstation. The specific capacity

Scheme 1 Schematic illustration of the fabrication processes of the hierarchical mesoporous Co₃O₄@ZnCo₂O₄ hybrid NWAs.

of the assembled devices was estimated from Equation (1), but m (g) represents the total mass of both the cathode and anode electrode materials. The energy density (E , W h kg⁻¹) and power density (P , W kg⁻¹) were calculated from $E = Q \times \Delta V / 2$ (Equation (2)) and $P = E / \Delta t$ (Equation (3)), respectively [36], where Q is the specific capacity, ΔV is the potential window of the device, and Δt is the discharge time.

RESULTS AND DISCUSSION

The schematic procedure for the fabrication of the hierarchical mesoporous Co₃O₄@ZnCo₂O₄ hybrid NWAs is illustrated in Scheme 1. Through a facile hydrothermal process with Co(NO₃)₂·6H₂O as raw materials and an annealing treatment, the Co₃O₄ NWAs on Ni foam were initially synthesized (step i). In the second hydrothermal process, the as-synthesized Co₃O₄ NWAs on Ni foam served as the templates. And ZnCo₂O₄ is further coated on the surface of Co₃O₄ NWAs through the hydrothermal process and annealing treatment to form the hierarchical mesoporous Co₃O₄@ZnCo₂O₄ hybrid NWAs (step ii).

The crystal structure and the phase purity of the as-prepared samples were studied by XRD. As shown in Fig. 1, it can be found that all the diffraction peaks can be indexed as Ni substrate (JCPDS card No. 04-0850), Co₃O₄ (JCPDS card No. 42-1467) and ZnCo₂O₄ (JCPDS card No. 23-1390), respectively. The relative intensities of Ni diffraction peaks decrease, indicating that the Ni foam was completely covered by the Co₃O₄ NWAs and Co₃O₄@ZnCo₂O₄ hybrid NWAs. EDS spectra (Fig. S1) were further investigated to determine the compositions of the as-synthesized samples. Zn element is not observed in the EDS spectrum of Co₃O₄ NWAs. The atomic ratio of Zn/Co in Co₃O₄@ZnCo₂O₄ hybrid NWAs is 7.23:27.61, which is much lower than the theoretical value of the atomic ratio of Zn/Co in ZnCo₂O₄, suggesting that the as-synthesized samples contain Co₃O₄ and ZnCo₂O₄.

The morphologies of as-fabricated hierarchical meso-

Figure 1 XRD patterns of Ni foam, hierarchical mesoporous Co_3O_4 NWAs and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs on Ni foam.

porous Co_3O_4 NWAs and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs were studied by SEM under different magnifications, as shown in Fig. 2. Compared to pure Ni foam (Fig. S2), it can be clearly seen that the Ni foam was uniformly covered by Co_3O_4 NWAs and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs (Fig. 2a, d), respectively. SEM images (Fig. 2b, c) of Co_3O_4 NWAs show needle-like shapes with a wire length of $\sim 3.5 \mu\text{m}$ and a diameter of $\sim 60 \text{ nm}$. After coating with ZnCo_2O_4 , the uniformity of the nanostructure is still well retained (Fig. 2e) and all hybrid NWAs are homogeneously aligned and separated apart. The diameters of $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ NWAs increase to $\sim 80 \text{ nm}$ (Fig. 2f).

The detailed nanostructures of the Co_3O_4 NWAs and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs were researched by TEM

and HRTEM. As illustrated in Fig. 3a, The Co_3O_4 NWA is highly porous due to the gas release during the annealing treatment. Furthermore, the Co_3O_4 NWAs are polycrystalline and composed of numerous interconnected nanoparticles, and the grain diameter is 6–10 nm. The abundant free space between particles not only offered more electroactive surface sites but also facilitated the uniform formation of $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid nanostructure. After coating with ZnCo_2O_4 , the diameter of $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ increases, suggesting that ZnCo_2O_4 indeed grew on the surface of Co_3O_4 NWAs (Fig. 3b) and the NWA was still porous. The specific surface area and pore size distributions of the Co_3O_4 NWAs and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs were tested by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods (Fig. S3). The Co_3O_4 NWAs have a specific surface area of $112.6 \text{ m}^2 \text{ g}^{-1}$, while the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs have the value of $128.7 \text{ m}^2 \text{ g}^{-1}$ and the pores in both samples are mainly in the mesoporous range ($\sim 7.5 \text{ nm}$). Such porous structures are believed to possess high structural integrity and sufficiently large surface area to stabilize the cycling stability. The HRTEM image of a single $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ NWA (Fig. 3c) clearly shows that the NWA is polycrystalline. The clearly resolved lattice fringes show an interplanar spacing of 0.47 and 0.24 nm, corresponding to the (111) and (311) planes of ZnCo_2O_4 , respectively. A representative STEM image of a single $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ NWA and the corresponding mappings for Zn, Co, and O elements (Fig. 3d–g) shows the element distribution in the NWA, suggesting that ZnCo_2O_4 nanoparticles are indeed attached to the Co_3O_4 NWAs by a second hydrothermal process to form the typical $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs.

Figure 2 SEM images of (a–c) hierarchical mesoporous Co_3O_4 NWAs and (d–f) $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs on Ni foam with different magnification.

Figure 3 Typical TEM images of (a) Co_3O_4 NWA, (b) $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWA, (c) HRTEM image and (d–g) EDS mapping images of the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWA.

The electrochemical performances of the Co_3O_4 NWAs electrode and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrode were evaluated in a three-electrode cell in 2 mol L^{-1} KOH aqueous electrolytes. Fig. 4a demonstrates the CV curves of Ni foam, as-fabricated Co_3O_4 NWAs and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs at a scan rate of 10 mV s^{-1} with a potential window from 0 to 0.6 V. Two pairs of redox peaks are observed for the Co_3O_4 electrode, which is due to the $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Co}^{3+}/\text{Co}^{4+}$ reactions [37]. For the hybrid electrode, the expanded peaks are mainly attributed to the $\text{Zn}^{2+}/\text{Zn}^{3+}$ reaction [38]. These results suggest that the two electrodes are the typical battery-type electrode materials. The CV integrated area of pure Ni foam is almost negligible compared with that of the Co_3O_4 and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid electrodes, revealing the almost no capacitance contribution of the current collector (Fig. S4). Obviously, the much larger CV-integrated area of the hybrid electrode than that of the Co_3O_4 electrode indicates a significant increase of the specific capacities. This similar result can also be obtained from GCD measurements (Fig. S5). At the same current density, $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrode has longer discharge time, suggesting a higher specific capacity. The high specific capacity of $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrode can be attributed to the unique hierarchical architectures of $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ active material, which enables sufficient exposure of Faraday-active components

[39–41].

Fig. 4b shows the representative CV curves of the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs obtained at different scan rates. At low scan rates, a pair of redox peaks observed indicates the existence of the Faradaic process, which is attributed to the reversible conversion [42]. The GCD curves of $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrode were obtained at the current density of 2–20 mA cm^{-2} (Fig. 4c and Fig. S6). It could be found that each curve has a good symmetry, implying excellent electrochemical reversibility and charge-discharge properties. The tiny voltage plateau confirms the redox reaction during charging and discharging, further suggesting the battery-type electrochemical behavior. The specific capacities of Co_3O_4 NWAs electrode and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrode at different current densities are compared in Fig. 4d. The specific capacities of the Co_3O_4 NWAs electrode are calculated to be 410.4, 401.6, 392.7, 384.9, 377.0, and 336.0 C g^{-1} at 2, 4, 6, 8, 10 and 20 mA cm^{-2} , respectively, according to Equation (1). Compared with the Co_3O_4 NWAs electrode, the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrode exhibits significantly enhanced specific capacities as high as 1,240.5, 1,186.3, 1,109.3, 1,048.0, 1,000.0 and 848.3 C g^{-1} at 2, 4, 6, 8, 10 and 20 mA cm^{-2} , respectively. With increasing the current density from 2 to 30 mA cm^{-2} , the capacity retention of the hybrid electrode of about 59.0% suggests an excellent rate capability. It is worth mentioning that the results in this work are also higher than those in other previous reports (Table S1).

To further characterize the electrochemical behavior of electrodes, EIS was tested and the corresponding curves of Co_3O_4 NWAs and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrodes were shown in Fig. 4e. The intercept of the high-frequency semicircle on the actual impedance axis (Z') represents the internal resistance (R_s). The R_s is the sum of the ionic resistance of the electrolyte, the intrinsic resistance of active materials and the contact resistance at the active material/current collector interface [42]. The diameter of the semicircle corresponds to the charge transfer resistance (R_{ct}) caused by Faradaic reactions. The fitted R_s and R_{ct} values of the electrodes agree well with that directly calculated from the Nyquist plot (Table S2). R_s values of 0.95 and 0.84 Ω can be respectively obtained and R_{ct} values of 1.04 and 0.91 Ω also can be obtained from the Co_3O_4 NWAs and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrodes. As expected, the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs show the smaller semicircle, demonstrating that this sample has a faster charge transfer process than the Co_3O_4 NWAs because of the synergistic effects of

Figure 4 (a) CV curves of Ni foam, the obtained Co_3O_4 NWAs and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrodes at a scan rate of 10 mV s^{-1} ; (b) CV curves of $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrode at different scan rates; (c) GCD curves of $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrode at different current densities; (d) specific capacities of Co_3O_4 NWAs and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrodes at different current densities; (e) EIS of Co_3O_4 NWAs and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrodes at open circuit potential (insert shows the equivalent circuit diagram) and (f) cycling performances of Co_3O_4 NWAs and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrodes at the current density of 10 mA cm^{-2} .

Co_3O_4 and ZnCo_2O_4 NWAs, which can enhance the conductivity and improve the ion transfer during the charge and discharge processes, compared to the bare Co_3O_4 NWAs electrode. The slope of the curves represents the Warburg impedance (W) in low frequency area, which shows the electrolyte diffusion in the electrode and proton diffusion in active materials. The $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrode shows a larger slope than Co_3O_4 NWAs electrode, implying the more excellent capacitive characteristics and the lower ion diffusion resistance [41,43–44]. The equivalent circuit diagram is shown in the inset of Fig. 4e. The cycling stabilities of Co_3O_4 NWAs and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrodes were carried out for 3,000 cycles at a current density of 10 mA cm^{-2} . As shown in Fig. 4f, the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrode exhibits a more excellent long-term stability with a capacitance retention of $\sim 90.9\%$ after 3,000 cycles, which is much higher than

$\sim 81.3\%$ capacitance retention for the Co_3O_4 NWAs electrode. The initial morphology of $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs was maintained and the NWAs were still found to densely cover the surface of Ni foam substrate after 3,000 cycles (Fig. S7). GCD curves for the first and the last 12 cycles (Fig. S8) show that all the curves did not show obvious differences and were symmetric regarding charge-discharge process, manifesting no significant structural degradation of $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs and further indicating that the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs showed excellent long-term electrochemical stability.

To assess the possibility of the as-obtained $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs for the practical application, an ASC was further fabricated by utilizing $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs as the cathode and AC as the anode. The AC electrode shows typical electric double-layer capacitance performance at -1.0 to 0.0 V (Fig. S9). Before as-

Figure 5 (a) CV curves of AC and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrodes at the scan rate of 10 mV s^{-1} ; (b) CV curves of $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4||\text{AC}$ ASCs at different scan rates; (c) GCD curves of $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4||\text{AC}$ ASCs at different current densities; (d) specific capacities at different current densities; (e) Ragone plots of the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4||\text{AC}$ ASCs and (f) cycling performance of $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4||\text{AC}$ ASCs at a current density of 5 A g^{-1} (inset shows a yellow LED powered by the device).

sembling the ASCs, the charge balance of the cathode and anode must be considered according to the charge balance theory ($q^+ = q^-$). The voltammetric charges (Q) are calculated based on the Equation (4) [36]: $Q = C \times \Delta V \times m$, where C is the specific capacity (C g^{-1}) of each electrode measured in a three electrode systems, and m is the mass of the electrode active materials.

According to the specific capacity values and the corresponding potential windows of the two electrodes, the mass ratio between $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs and AC electrode is approximately 0.21 in the ASCs. Fig. 5a shows the CV curves of AC and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrodes in a three-electrode cell at a scan rate of 10 mV s^{-1} . A nearly rectangular CV curve of AC electrode within a voltage window of -1.0 to 0 V indicates a typical electric double-layer capacitance behavior since no redox peaks are observed. As for $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrode in the voltage window from 0 to 0.6 V , the redox peaks are clearly observed, owing to the typical Faraday reaction. The total voltage of the supercapacitor can be expressed as the sum of the potential range for the AC and $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs electrodes and thus the whole voltage windows of the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4||$

AC ASCs can be extended to 1.6 V . A smaller potential window cannot contain significant pseudocapacitance, whereas an excessively higher potential window would cause O_2 evolution (Fig. S10). Therefore, a typical CV curve originating from the combination of pseudocapacitance and electric double-layer capacitance can be obtained at a voltage window of 0 – 1.6 V . Fig. 5b shows the typical CV curves of the assembled $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4||\text{AC}$ ASCs from 0 to 1.6 V at various scan rates from 5 to 50 mV s^{-1} . When the scan rate increases, the shapes of the CV curves remain the similar shape, indicating the desirable fast charge-discharge property for power devices. Fig. 5c shows the GCD curves of the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4||\text{AC}$ ASCs at different current densities from 1 to 10 A g^{-1} with a voltage window of 0 – 1.6 V . GCD curves are almost symmetrical to its corresponding charge curves, indicating good capacitive behavior for the ASCs. The specific capacities of the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4||\text{AC}$ ASCs are 168.0 , 154.1 , 143.1 , 134.1 , 126.1 , 118.3 , 107.2 and 96.0 C g^{-1} at current densities of 1 , 2 , 3 , 4 , 5 , 6 , 8 and 10 A g^{-1} , respectively, as shown in Fig. 5d. The $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4||\text{AC}$ ASCs exhibited a high retention rate of 57.1% , even when operated at a current density of 10 A g^{-1} , indicating the

excellent rate capability of the device.

The Ragone plots of the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4\|\text{AC}$ ASCs calculated from the GCD measurement at different current densities are presented in Fig. 5e. The ASCs can deliver a high energy density of 37.3 W h kg^{-1} at a power density of 800 W kg^{-1} and still maintain as high as 21.3 W h kg^{-1} while at a high power density of 8 kW kg^{-1} , which is higher than previously reported ASCs [45–49]. The cycling performance of the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4\|\text{AC}$ ASCs was performed at a current density of 5 A g^{-1} (Fig. 5f). After 6,000 cycles, the specific capacity was still retained 96.3%, indicating the excellent cycling performance of the device. The ASC was further assembled to demonstrate the practical application. After charging 27 s, the yellow LED indicator can be powered for about 5 min, suggesting that the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4\|\text{AC}$ ASCs are very promising candidates for supercapacitor applications.

CONCLUSIONS

In summary, hierarchical mesoporous $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs on Ni foam were prepared through a two-step hydrothermal process associated with successive annealing treatment. The electrochemical performances of the as-synthesized hierarchical hybrid electrode were measured, and the specific capacity is 1240.5 C g^{-1} at a current density of 2 mA cm^{-2} , the good rate capability is 59.0% when the current density increases from 2 to 30 mA cm^{-2} and the cycling stability is 90.9% after 3,000 cycles at a high current density of 10 mA cm^{-2} . For more practical application, the ASC was fabricated using the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ NWAs as the cathode and the AC as the anode. The device showed a high capacity of 168 C g^{-1} at a current density of 1 A g^{-1} , good cycling stability in a wide potential window of 0–1.6 V (96.3% retention after 6,000 cycles), and also delivered an excellent energy density of 37.3 W h kg^{-1} at a power density of 800 W kg^{-1} . Therefore, the $\text{Co}_3\text{O}_4@\text{ZnCo}_2\text{O}_4$ hybrid NWAs are expected to be a promising candidate for the application in high-performance electrochemical capacitors, and the as-fabricated ASCs also show great potential in the development of energy storage devices with high energy and power densities.

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Author contributions Li M, Yang W and Yu Y designed the research. Li M fabricated the materials and devices, analyzed the results, and wrote the manuscript with support from Huang Y. Yu Y and Yang W supervised the project and revised the manuscript. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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用于高性能非对称超级电容器电极的泡沫镍负载分层介孔 $\text{Co}_3\text{O}_4@ \text{ZnCo}_2\text{O}_4$ 混合纳米线阵列

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摘要 本文采用两步水热法和连续的退火处理过程, 制备了分层介孔 $\text{Co}_3\text{O}_4@ \text{ZnCo}_2\text{O}_4$ 复合纳米线阵列。所制备的 $\text{Co}_3\text{O}_4@ \text{ZnCo}_2\text{O}_4$ 复合纳米线阵列具有优异的电化学性能, 在 2 mA cm^{-2} 的电流密度下具有高达 1240.5 C g^{-1} 的比容量。当电流密度升高至 30 mA cm^{-2} 时, 比容量保持率为59.0%, 甚至在 10 mA cm^{-2} 的电流密度下循环3000圈, 比容量仅下降9.1%。将其与活性炭组装成非对称超级电容器, 可以在 1 A g^{-1} 的电流密度下表现出 168 C g^{-1} 的比容量。当功率密度为 800 W kg^{-1} 时, 能量密度为 37.3 W h kg^{-1} 。 $\text{Co}_3\text{O}_4@ \text{ZnCo}_2\text{O}_4$ 复合纳米阵列在储能领域具有广阔的应用前景。